Title: HYDROGEN STORAGE MATERIAL BASED ON A MULTILAYERED CORE/SHELL STRUCTURE
Inventor's Name: Peter C. EKLUND, et al.
Application No.: New Application
Docket No.: 025756-00003

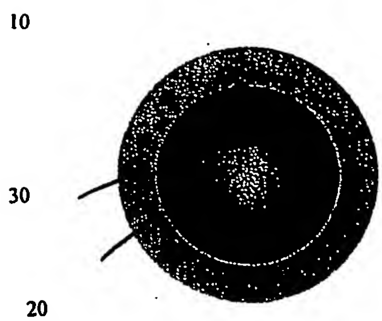

FIG. 1A

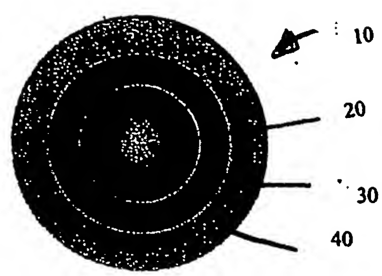

FIG. 1B

Title: HYDROGEN STORAGE MATERIAL BASED ON A MULTILAYERED CORE/SHELL STRUCTURE
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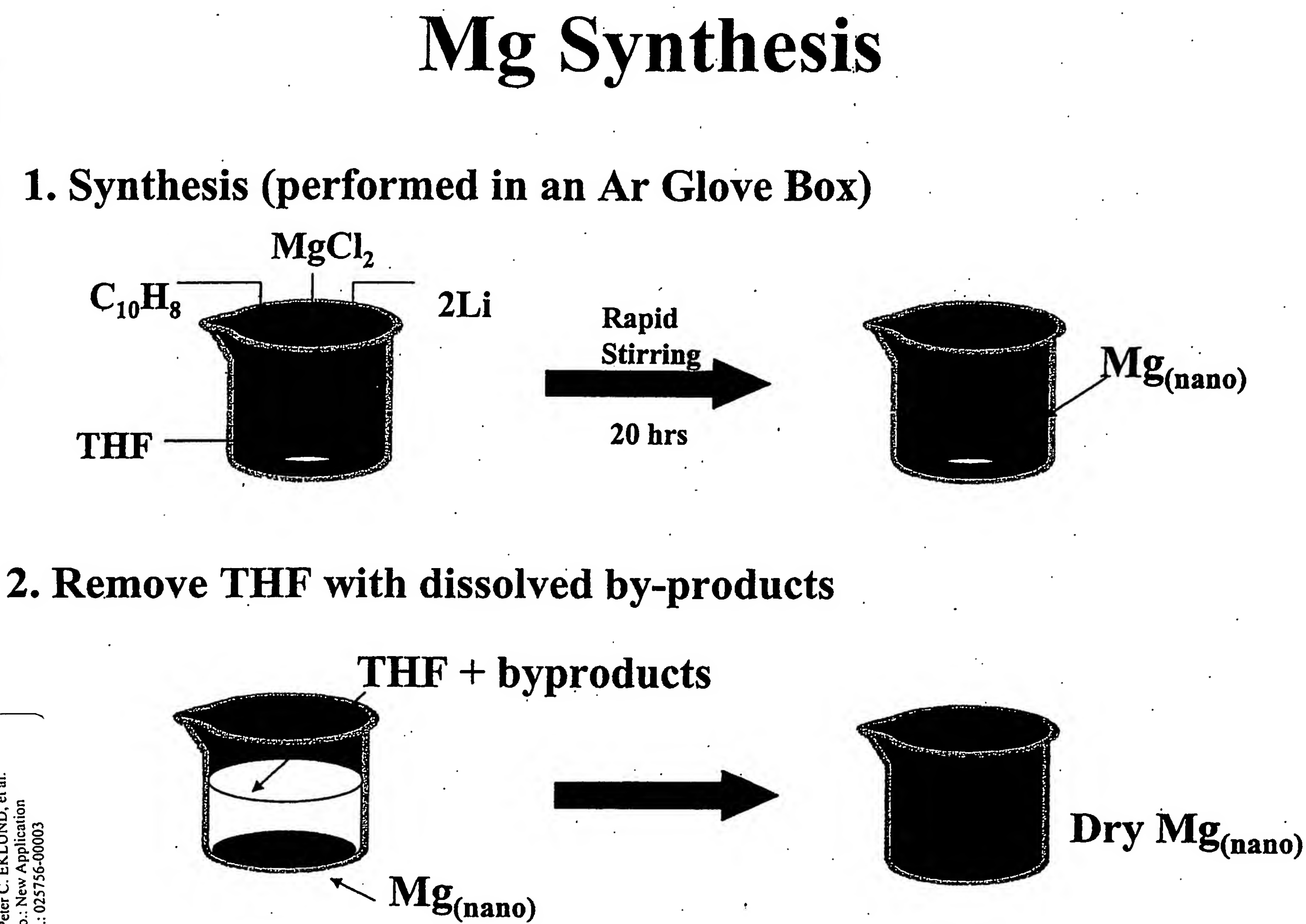

FIG. 2

Synthesized Mg

FIG. 3

Sample	Amount Made	XRD crystallite size (Scherrer equation)*
Mg 1-2	0.198g	23nm
Mg 1-10	0.4g	Used in Pd capping
Mg 1-13	0.4g	37nm
Mg 1-18	0.2g	34nm
Mg 1-41	0.2g	Used for Co capping
Mg 1-51	0.4g	33nm
Mg 1-57a	0.5g	25nm
Mg 1-57b	0.5g	Still in dry box
Mg 1-57c	0.5g	Almost amorphous

$$*t = [(0.9)(0.154)]/[(\beta)(\cos\theta)]$$

t = crystallite size in nm
β = full width half max
θ = Bragg angle

Klug and Alexander, 1950

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As Synthesized Mg XRD

XRD of Mg 1-13 sample matches that of an indexed Mg pattern
Material is coated with amorphous sp^2 carbon allowing it to be stable in air

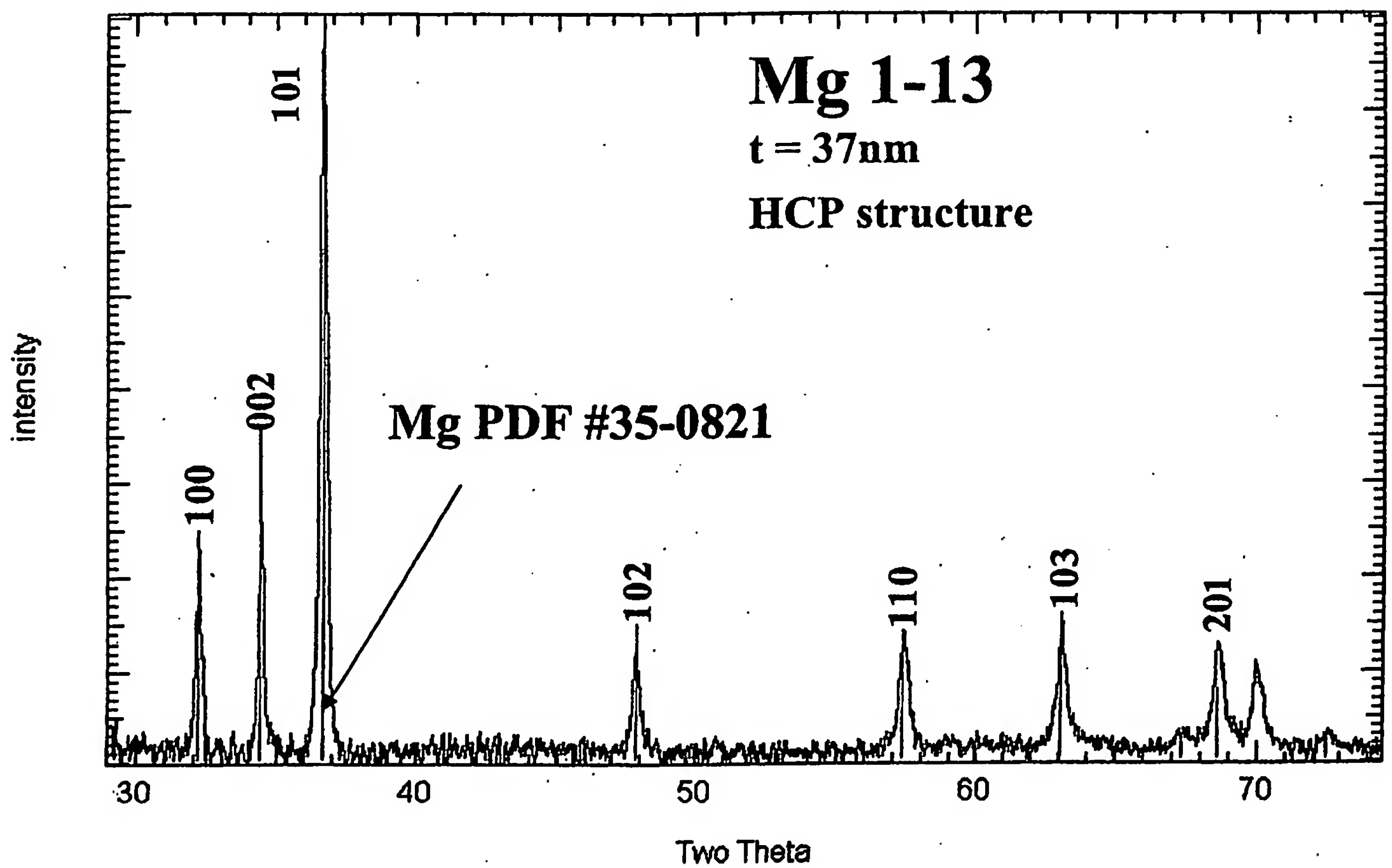

FIG. 4

Still Mg Metal!

Mg 1-13 sample was stable in atmospheric conditions for 3 months

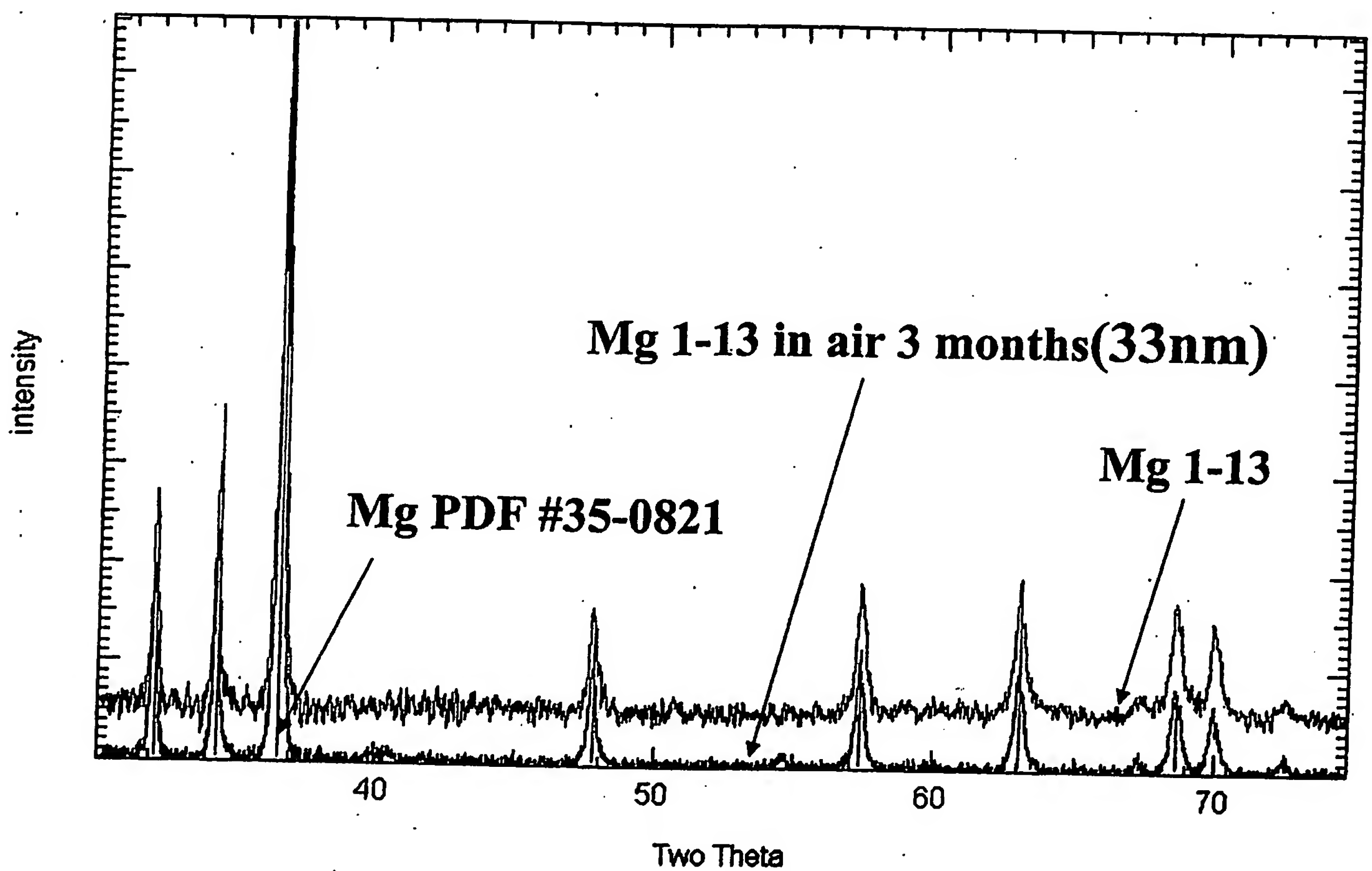

FIG. 5

Title: HYDROGEN STORAGE MATERIAL BASED ON A MULTILAYERED CORE/SHELL STRUCTURE
Inventor's Name: Peter C. EKLUND, et al.
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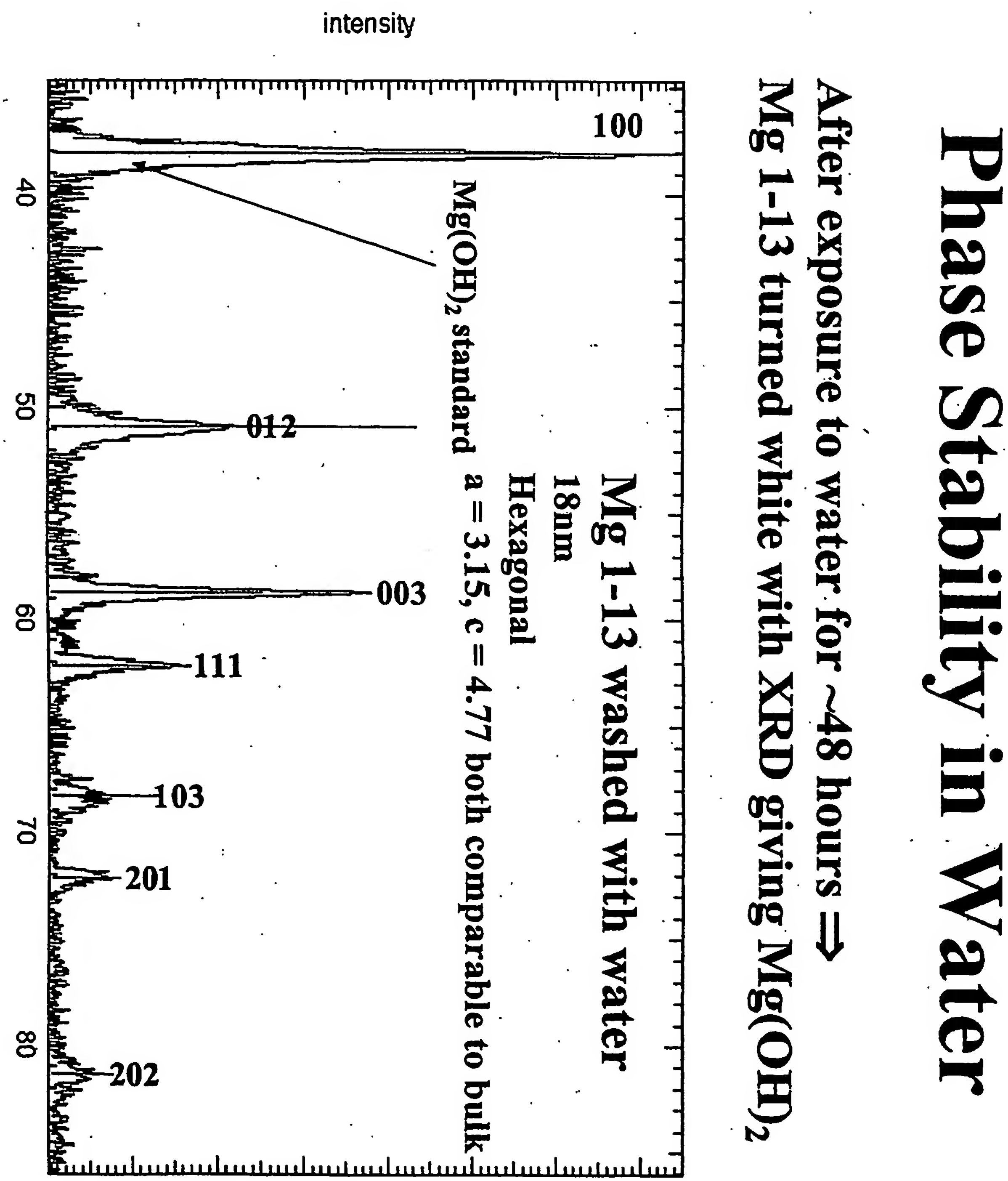


FIG. 6

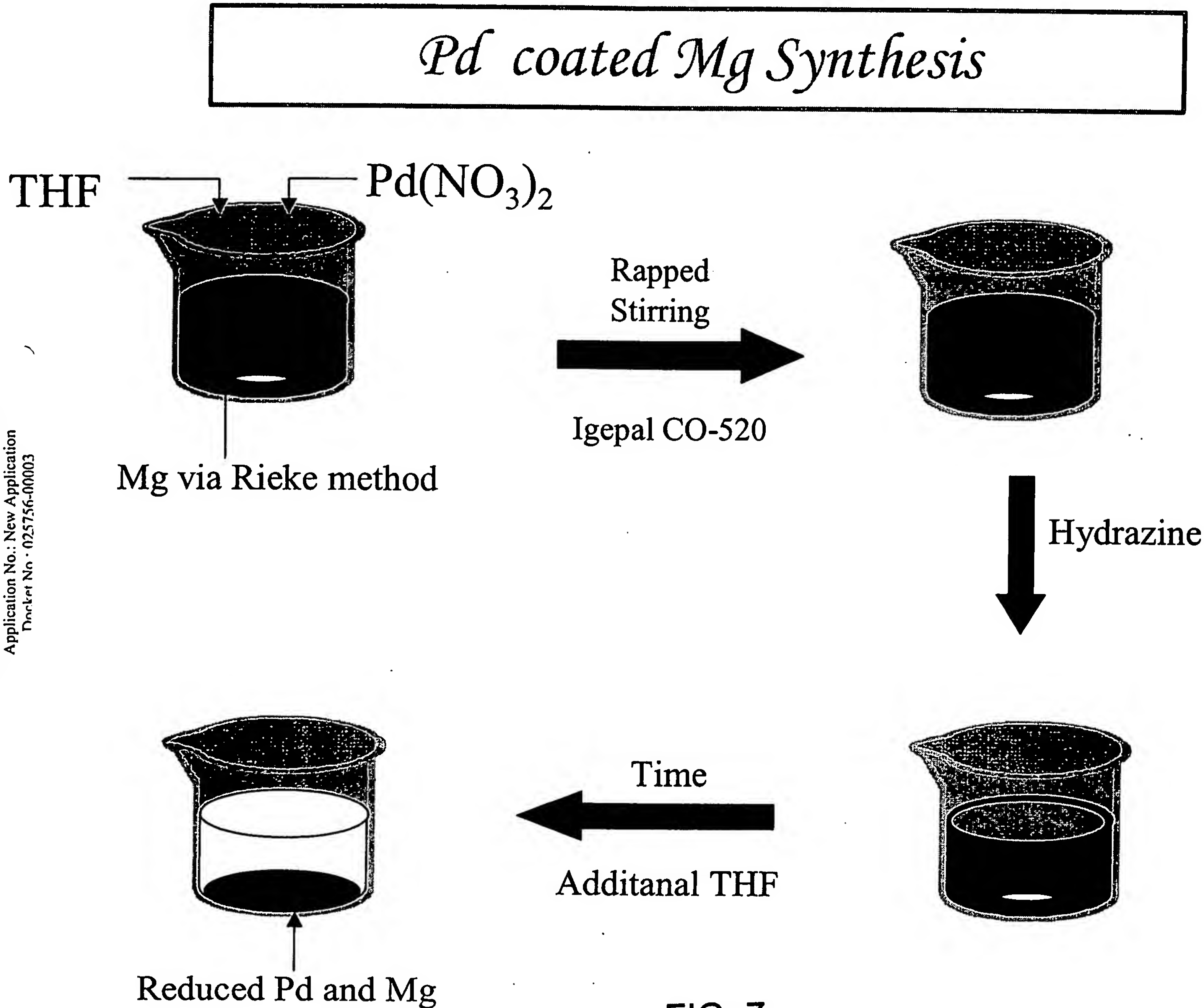

Pd coated Mg Synthesis
THF
$Pd(NO_3)_2$
Mg via Rieke method
Rapped Stirring
Igepal CO-520
Hydrazine
Time
Additanal THF
Reduced Pd and Mg

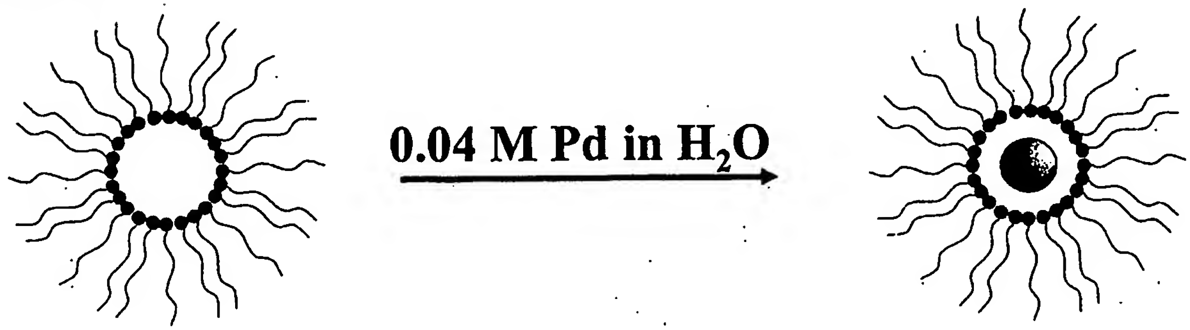
FIG. 7

Spherical nPd

1) Micelle Formation

Igepal™

cyclohexane



2) Reduction of Pd^{+2} using Hydrazine Hydrate ($H_2NNH_2 \bullet xH_2O$)

$$2Pd^{+2}\,(aq) + N_2H_4(aq) + 4OH^-\,(aq) \rightarrow 2Pd^0(s) + N_2(g) + 4H_2O$$

3) Break the Micelle and collect the Pd with ethanol

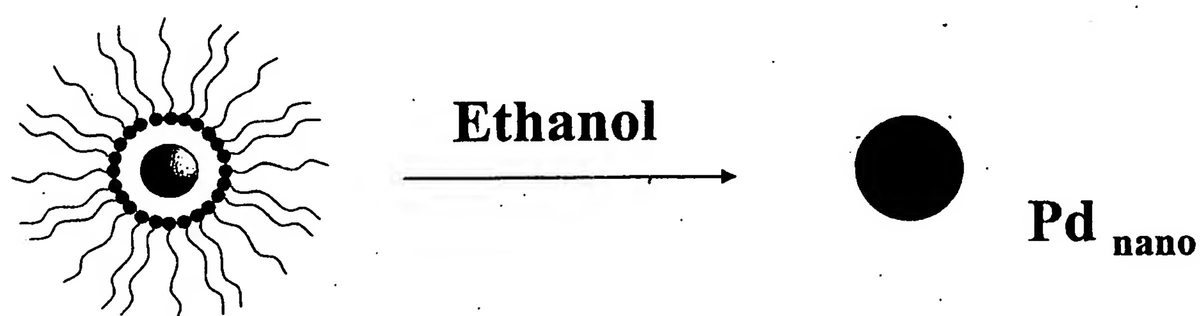


FIG. 8

FIG. 9

Controlling The Size

The size of the Pd spherical particle is dependent on the mole% ratio of surfactant (Igapal) to water often referred to as the R value.

$$R = [\text{water}]/[\text{surfactant}]$$

The larger the R value the larger the radius of the particle

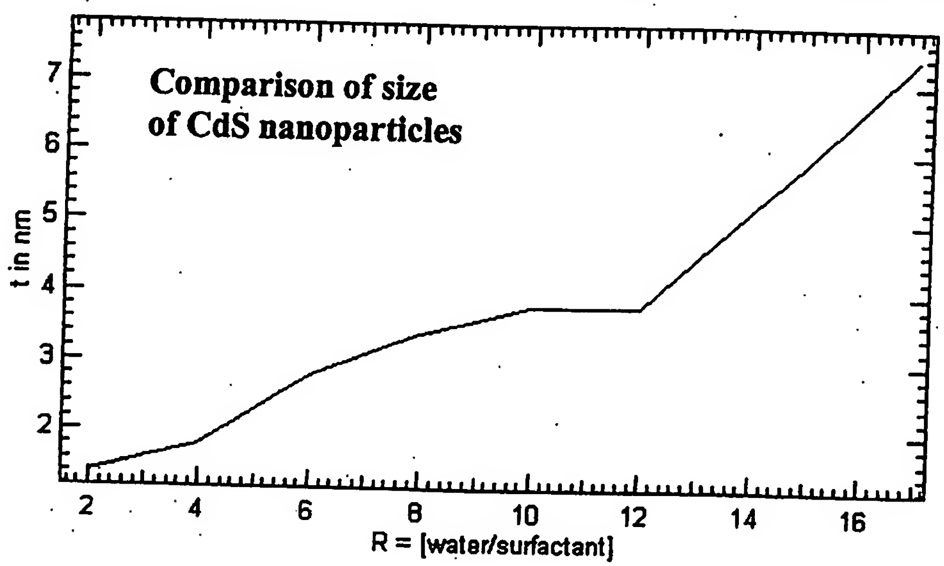


FIG. 10

Spherical Pd Synthesized to Date

Sample	R value	Amount made	Particle size*
Pd 1-62	8	1.3mg	
Pd 1-67	6	4mg	
Pd 1-68-1	1	2mg	
Pd 1-68-2	2	4mg	
Pd 1-69-1	1	.67mg	
Pd 1-68-2	2	1.35mg	
Pd 1-69-6	6	12.3mg	
Pd 1-69-8	8	16.32mg	
Pd 1-70-7	7	19mg	
Pd 1-70-9	9	30.5mg	~9nm
Pd 1-71	9	61mg	
Pd 1-73	5	63.6mg	
Pd 1-74-3	3	61mg	
Pd 1-74-7	7	71mg	
Pd 1-91-6	6	81.4mg	5nm
Pd 1-91-8	8	108.5mg	4nm
Pd 1-96	7	399mg	
Pd 1-100	25	84.8mg	6nm

*By Scherrer equation

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DF TEM Spherical Pd

Pd 1-91 R=8; t=4nm

FIG. 11

Title: HYDROGEN STORAGE MATERIAL BASED ON A MULTILAYERED CORE/SHELL STRUCTURE
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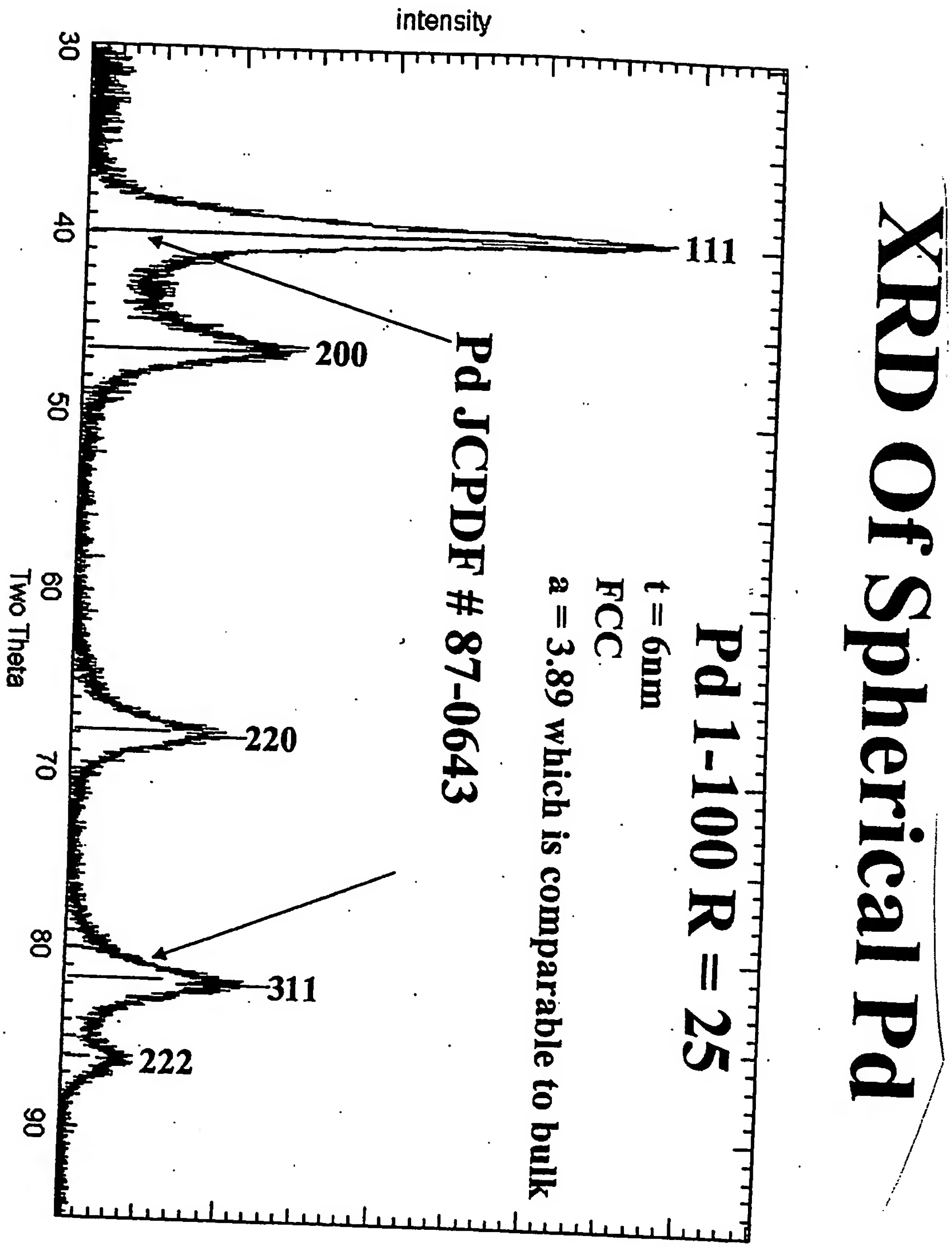
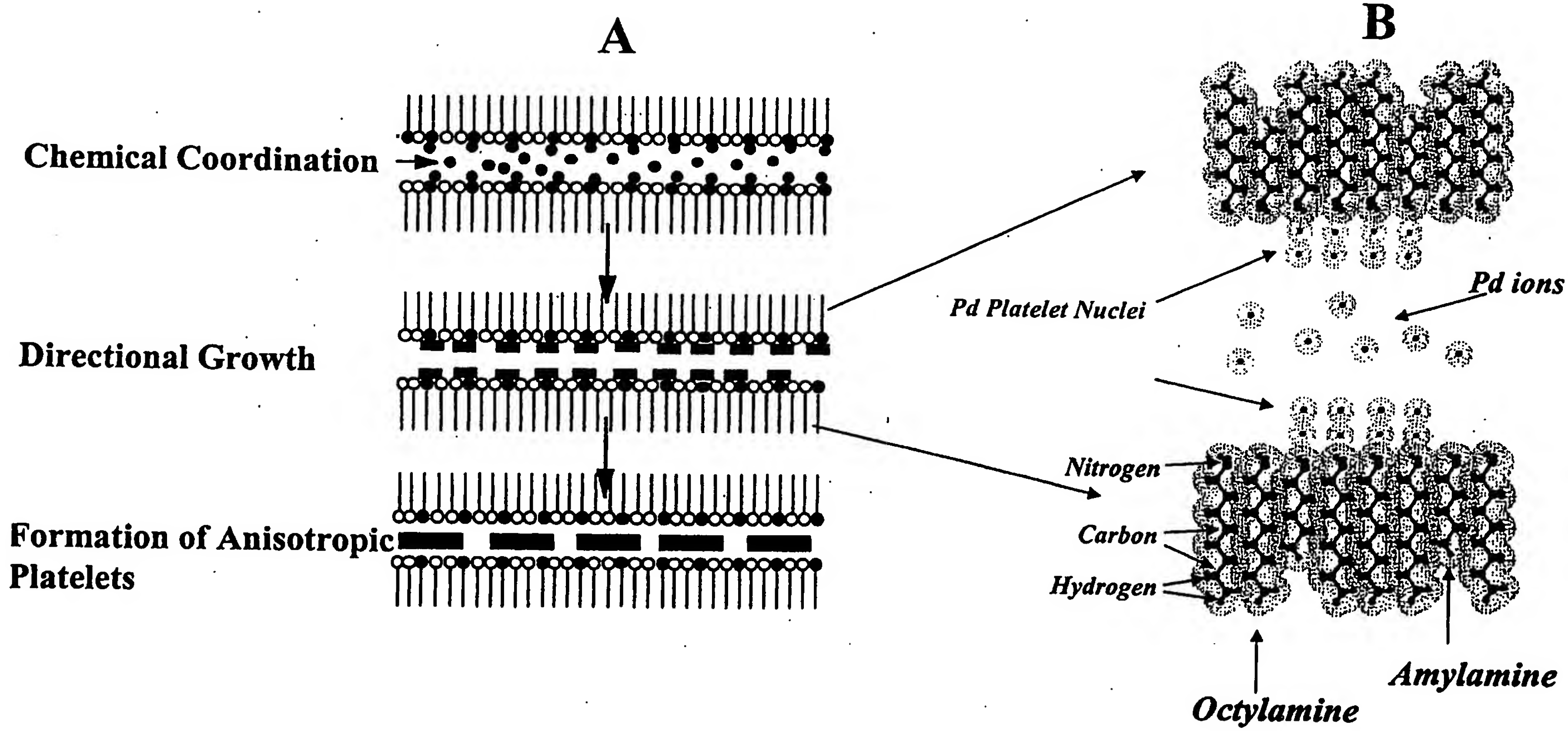


FIG. 12

FIG. 13

Synthetic Approach For Platelet Pd Particles

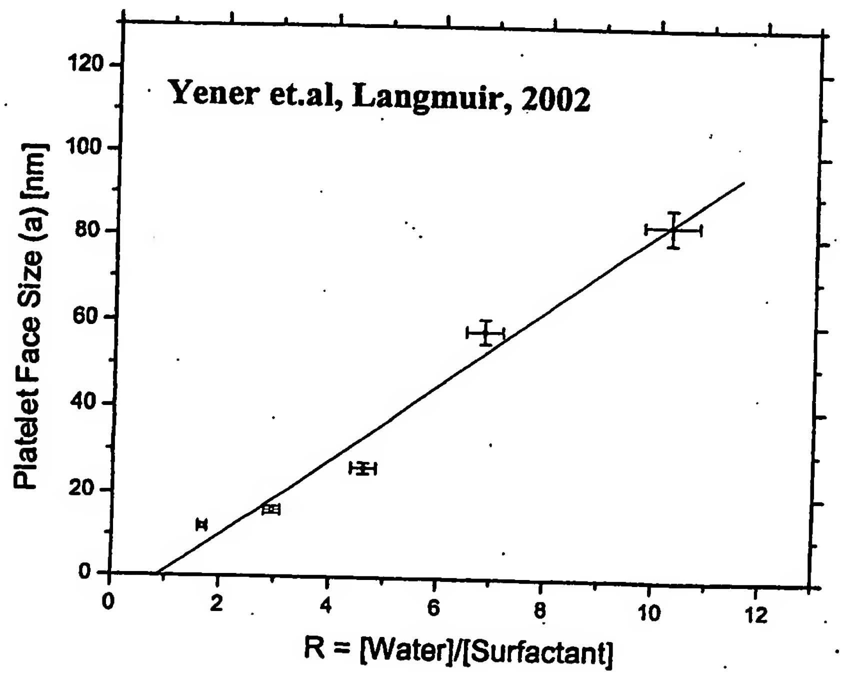


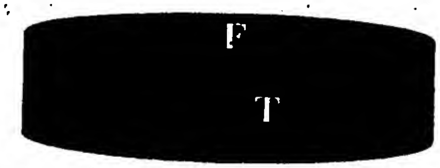
Platelet Size Control

R = [Water]/[Surfactant]

Surfactant = Octylamine + 5% Amylamine
$[CH_3(CH_2)_7NH_2]$ $[CH_3(CH_2)_4NH_2]$

The platelet face size (a) as a function of R.





F = Face
T = Thickness

FIG. 14

Platelets Made

Sample	R Value	Amount Made	F*	T*
Pd 1-75	6.8	20.4mg		
Pd 1-77	20.4	228mg		
Pd 1-80-3.4	3.4	66mg		
Pd 1-80-1.7	1.7	33mg		
Pd 1-86	10.2	236mg		
Pd 1-91-8.5	8.5	212mg		
Pd 1-91-6.8	6.8	254mg		
Pd 2-5-1.7	1.7	21.2		
Pd 2-5-3.4	3.4	21.2		
Pd 2-5-6.8	6.8	21.2	33nm	2nm
Pd 2-5-8.5	8.5	21.2		
Pd 2-5-10.2	1.2	21.2	150nm	6nm
Pd 2-5-20.4	20.4	21.2		
Pd 2-8a	10.2	21.2	130nm	8nm
Pd 2-8b (AA)	10.2	21.2	80nm	1.7nm

*

FIG. 15

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Materials Synthesized

nMg

Sample	Amount Made
Mg 1-2	0.198g
Mg 1-10	0.4g
Mg 1-13	0.4g
Mg 1-18	0.2g
Mg 1-41	0.2g
Mg 1-51	0.4g
Mg 1-57a	0.5g
Mg 1-57b	0.5g
Mg 1-57c	0.5g

Spherical nPd

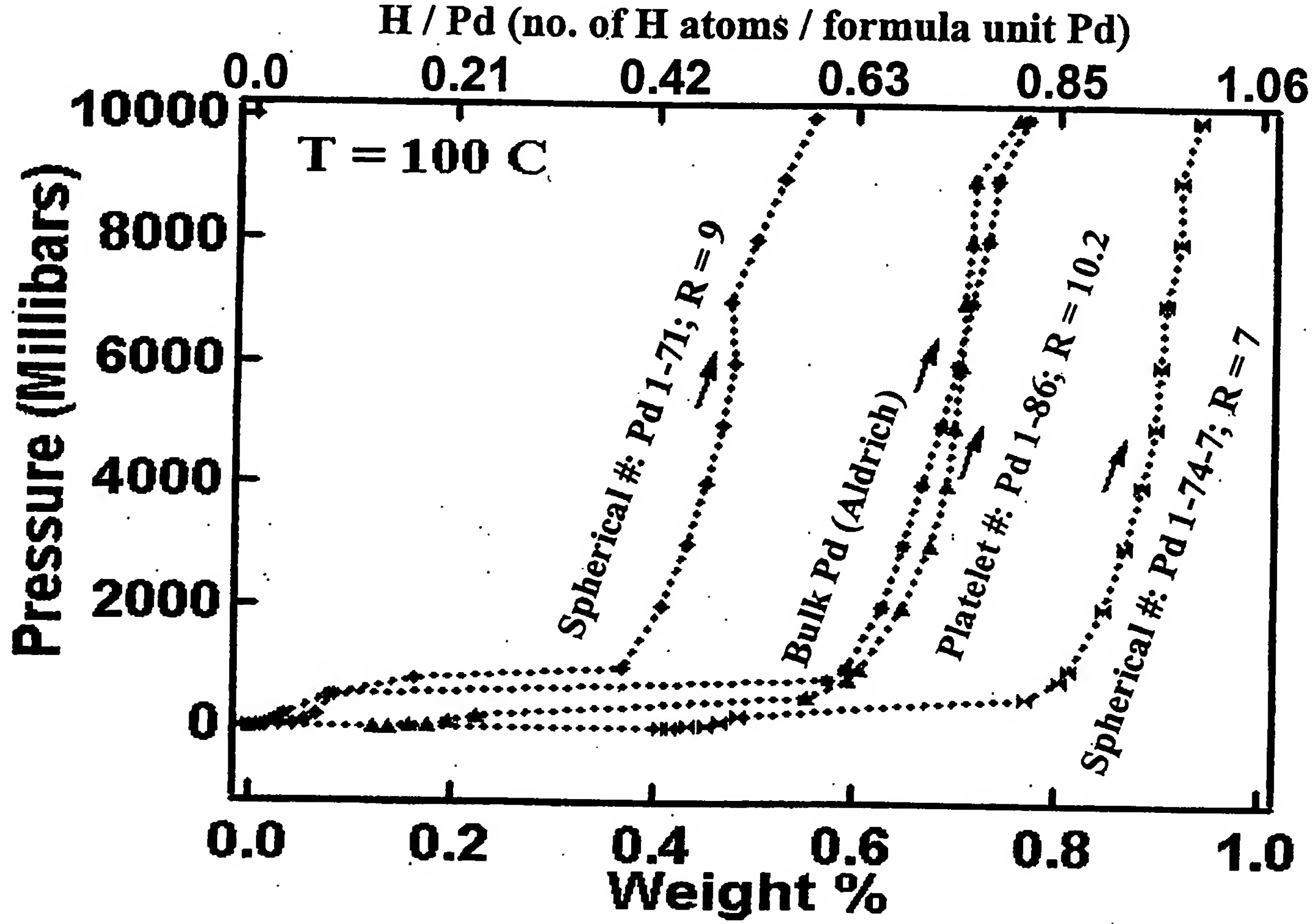
Sample	R Value	Amount Made
Pd 1-62	8	1.3mg
Pd 1-67	6	4mg
Pd 1-68-1	1	2mg
Pd 1-68-2	2	4mg
Pd 1-69-1	1	.67mg
Pd 1-68-2	2	1.35mg
Pd 1-69-6	6	12.3mg
Pd 1-69-8	8	16.32mg
Pd 1-70-7	7	19mg
Pd 1-70-9	9	30.5mg
Pd 1-71	9	61mg
Pd 1-73	5	63.6mg
Pd 1-74-3	3	61mg
Pd 1-74-7	7	71mg
Pd 1-91-6	6	81.4mg
Pd 1-91-8	8	108.5mg
Pd 1-96	7	399mg
Pd 1-100	25	84.8mg

Platelet nPd

Sample	R Value	Amount Made
Pd 1-75	6.8	20.4mg
Pd 1-77	20.4	228mg
Pd 1-80-3.4	3.4	66mg
Pd 1-80-1.7	1.7	33mg
Pd 1-86	10.2	236mg
Pd 1-91-8.5	8.5	212mg
Pd 1-91-6.8	6.8	254mg
Pd 2-5-1.7	1.7	21.2
Pd 2-5-3.4	3.4	21.2
Pd 2-5-6.8	6.8	21.2
Pd 2-5-8.5	8.5	21.2
Pd 2-5-10.2	1.2	21.2
Pd 2-5-20.4	20.4	21.2
Pd 2-8a	10.2	21.2
Pd 2-8b (AA)	10.2	21.2

FIG. 16

Adsorption Isotherms of Palladium NanoParticles and Bulk Sample at 100°C



Bulk sample particle size: 1.0 – 1.5 Microns
Spherical particles: **R** = 7 (5nm) and **R = 9(8nm);**
Platelets **R=10.2 (8nm thick)**

FIG. 17

Comparison of TGA Evaluations at 100C for Nano and Bulk Samples

Sample	Knee for H/Pd Ratio	Plateau Onset (Wt %)	Estimated Adsorption Rate* (H/Pd/min)	Estimated Desorption Rate* (H/Pd/min)
Pd 1-74-7 R = 7 (4-5 nm Spheres)	~ 0.78	~ 0.47	~0.01	~0.005
Pd 1-86 R = 10.2 (8 nm thick Platelets)	~ 0.65	~ 0.2	0.007	0.003
Bulk (1.0 – 1.5μm)	~ 0.6	~ 0.08	0.005	0.002

* Possibly affected by sintering

FIG. 18

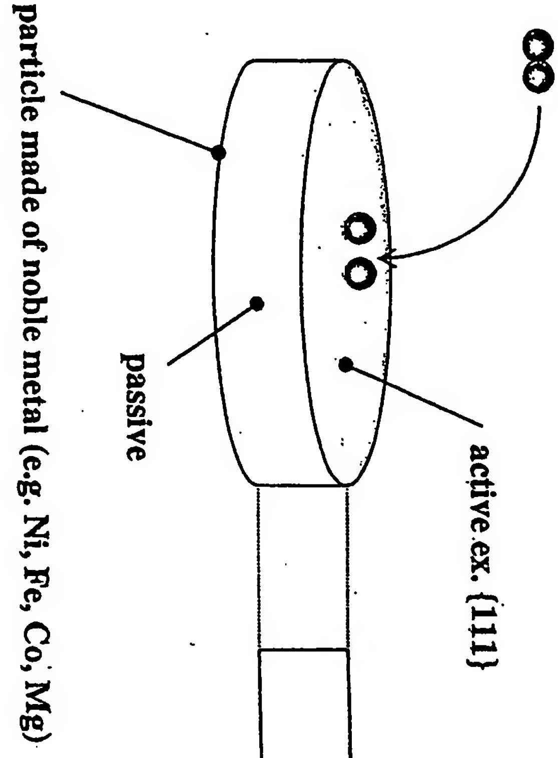

active ex. {111}
passive
platelet particle made of noble metal (e.g. Ni, Fe, Co, Mg)

FIG. 19

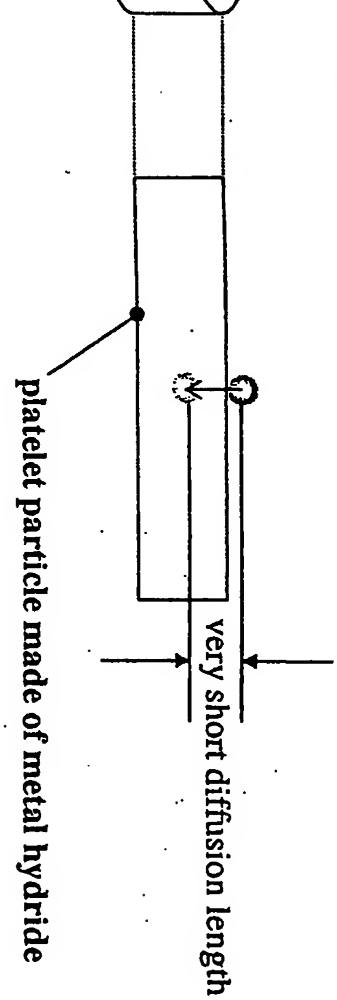

very short diffusion length
platelet particle made of metal hydride

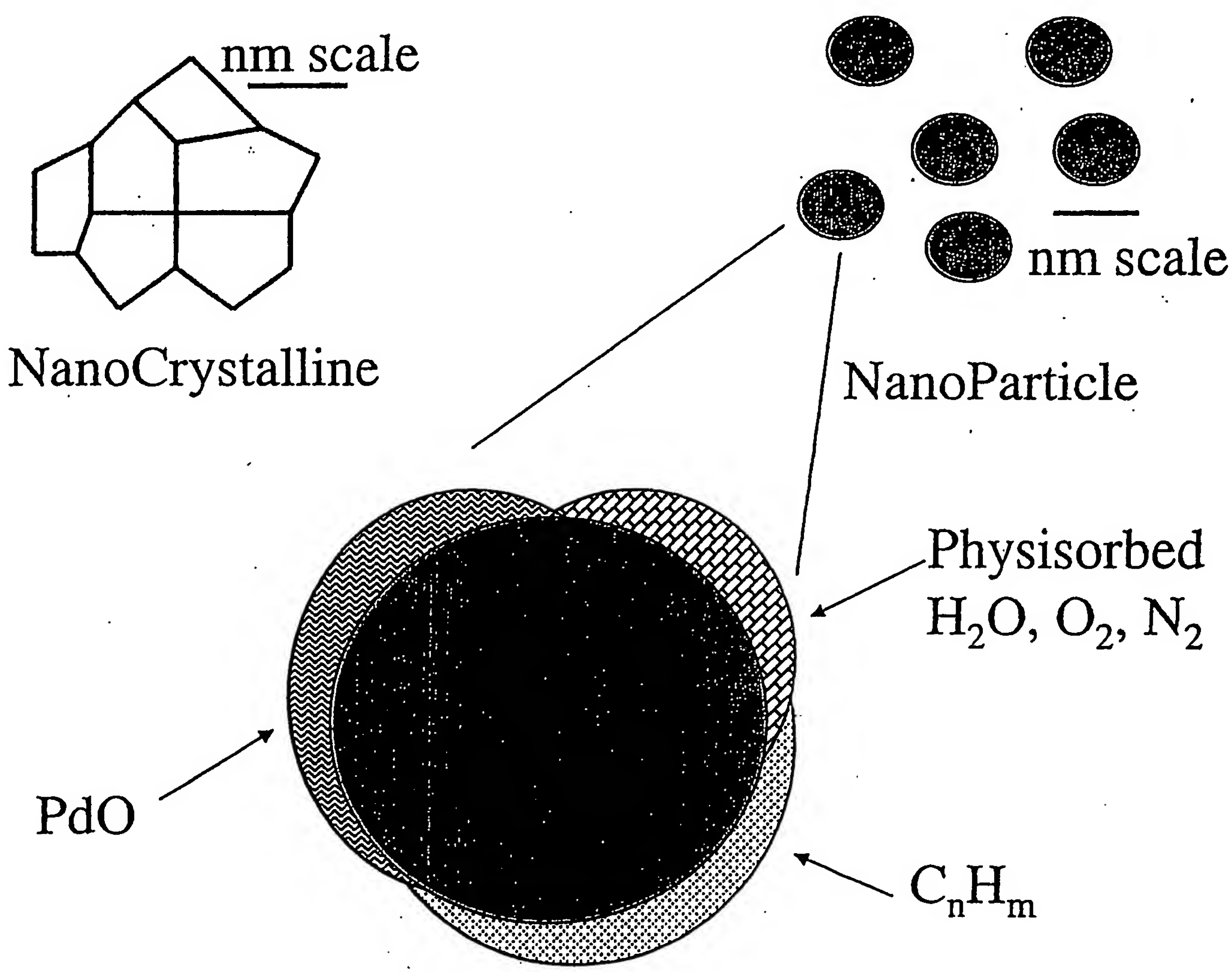
FIG. 20

FIG. 21

TGA Compositional Analysis

Sample	Pd in sample	Wt.%Pd as PdO in sample	Wt.% Carbon	η corr. factor
Spherical				
Pd 2-35 R=2 (4nm)	95.34%	0%	2.37%	1.05
Pd 2-71 R=8	96.16%	0%	0.05%	1.04
Platelet				
Pd 2-65-10 R=10 (327nm X 2.8nm to 109nm X 1.5nm)	87.26%	0%	0.08%	1.15
Pd 2-65-7 R=7 (82nm X 1.3nm)	94.69%	0%	0.17%	1.06

FIG. 22 **NanoCrystalline vs NanoParticle**



Title: HYDROGEN STORAGE MATERIAL BASED ON A MULTILAYERED CORE/SHELL STRUCTURE
Inventor's Name: Peter C. EKLUND, et al.
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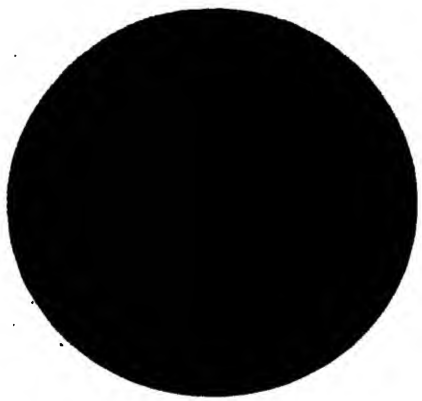
FIG. 23 . Effect of morphology on particle packing

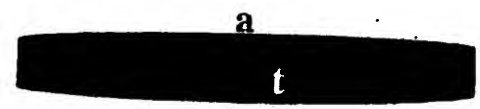
Spherical



r ~ 3-50 nm

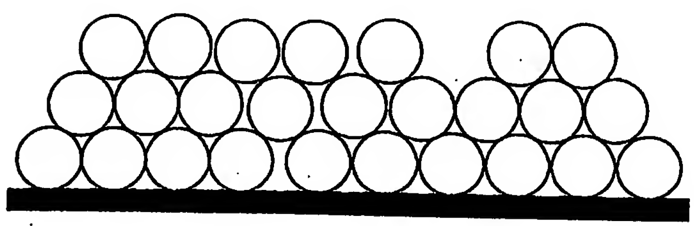
vs

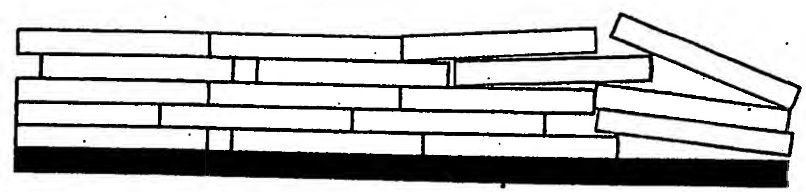
Platelet



t ~ 1-200 nm
a/t ~ 10-100

Particle Packing Characteristics





Title: HYDROGEN STORAGE MATERIAL BASED
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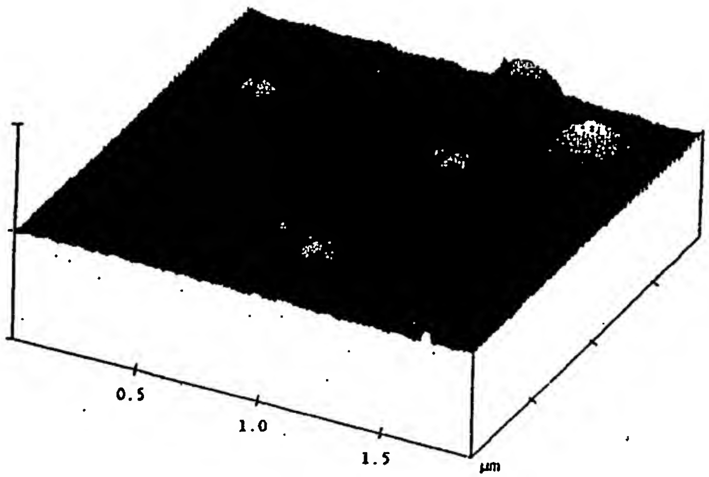
STRUCTURE
Inventor's Name: Terumi FURUTA, et al.
Application No.: New Application
Docket No.: 025756-00003

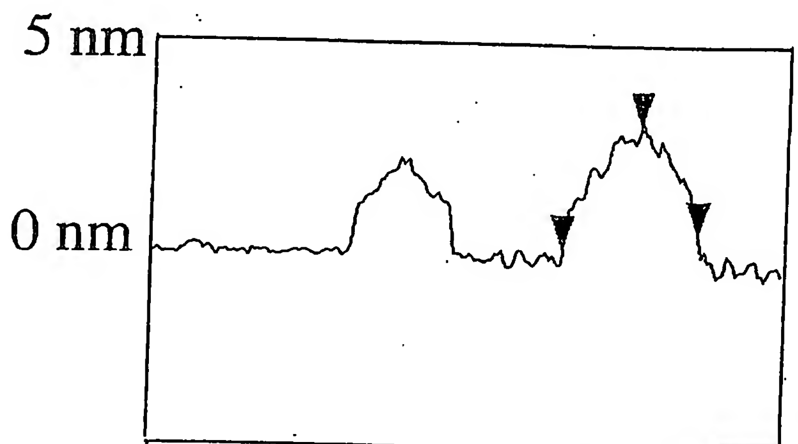
FIG. 24 HRTEM of Platelet nanoPd

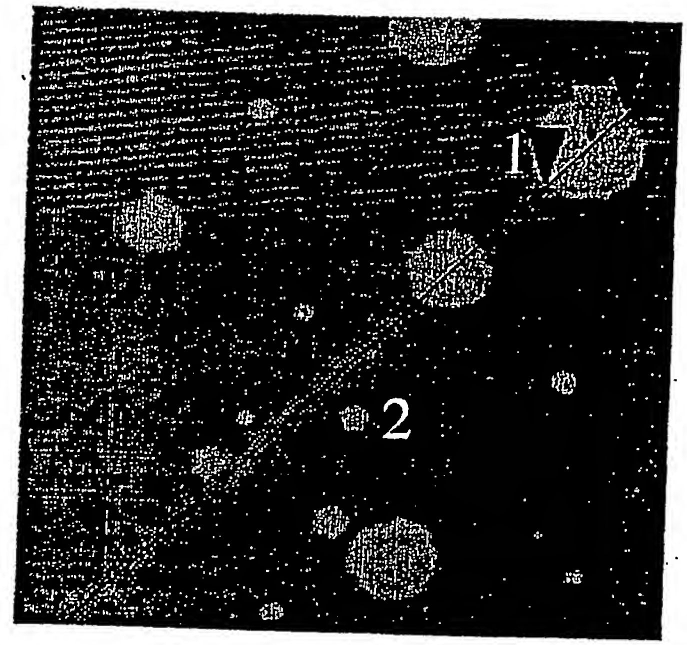
Moire fringes

FIG. 25

AFM of Platelet nanoPd







(1) 327nm X 2.8nm
(2) 109nm X 1.5nm

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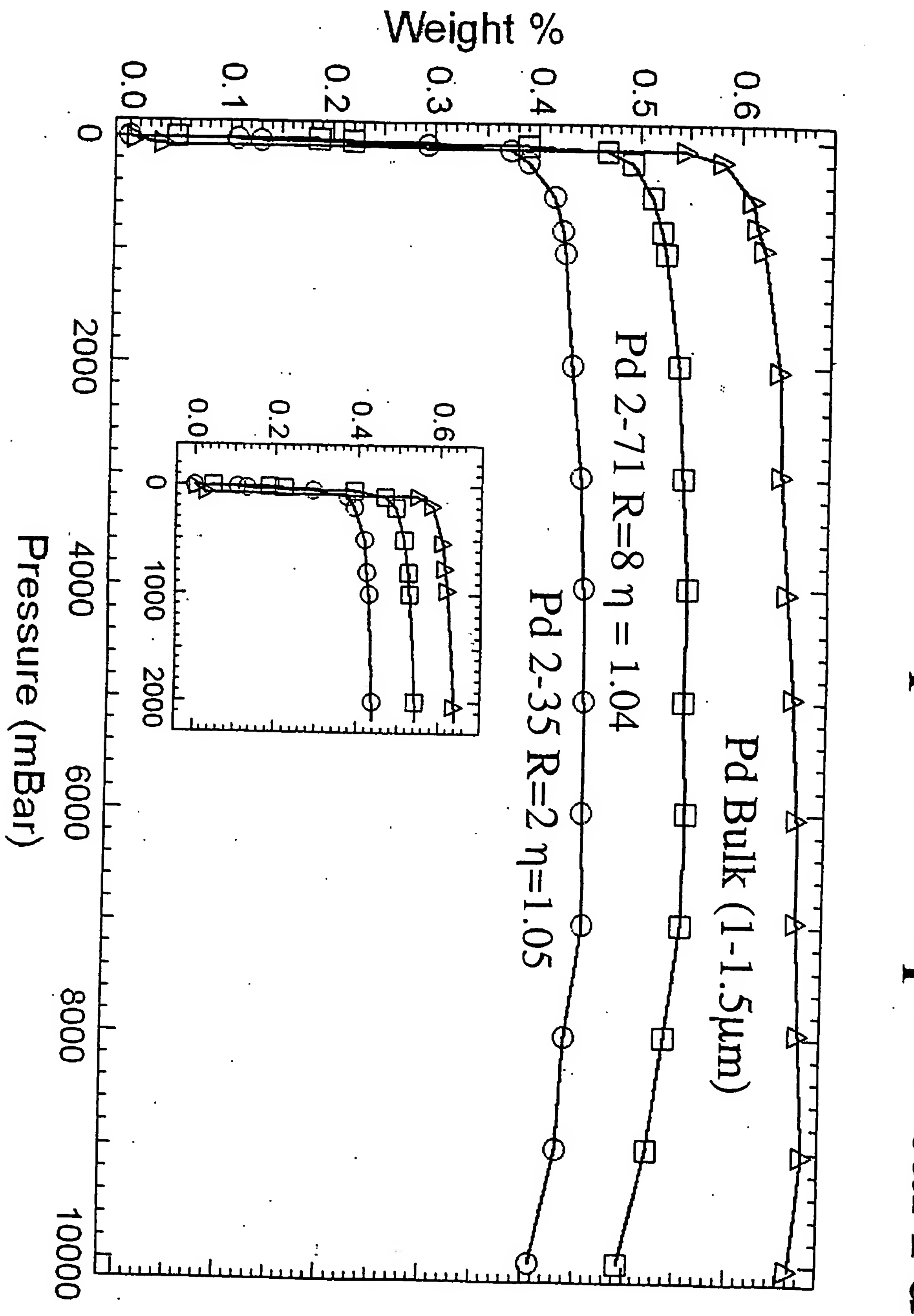
FIG. 26 H Adsorption of Spherical Pd



Title: HYDROGEN STORAGE MATERIAL BASED ON A MULTILAYERED CORE/SHELL STRUCTURE
Inventor's Name: Peter C. EKLUND, et al.
Application No.: New Application
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FIG. 27

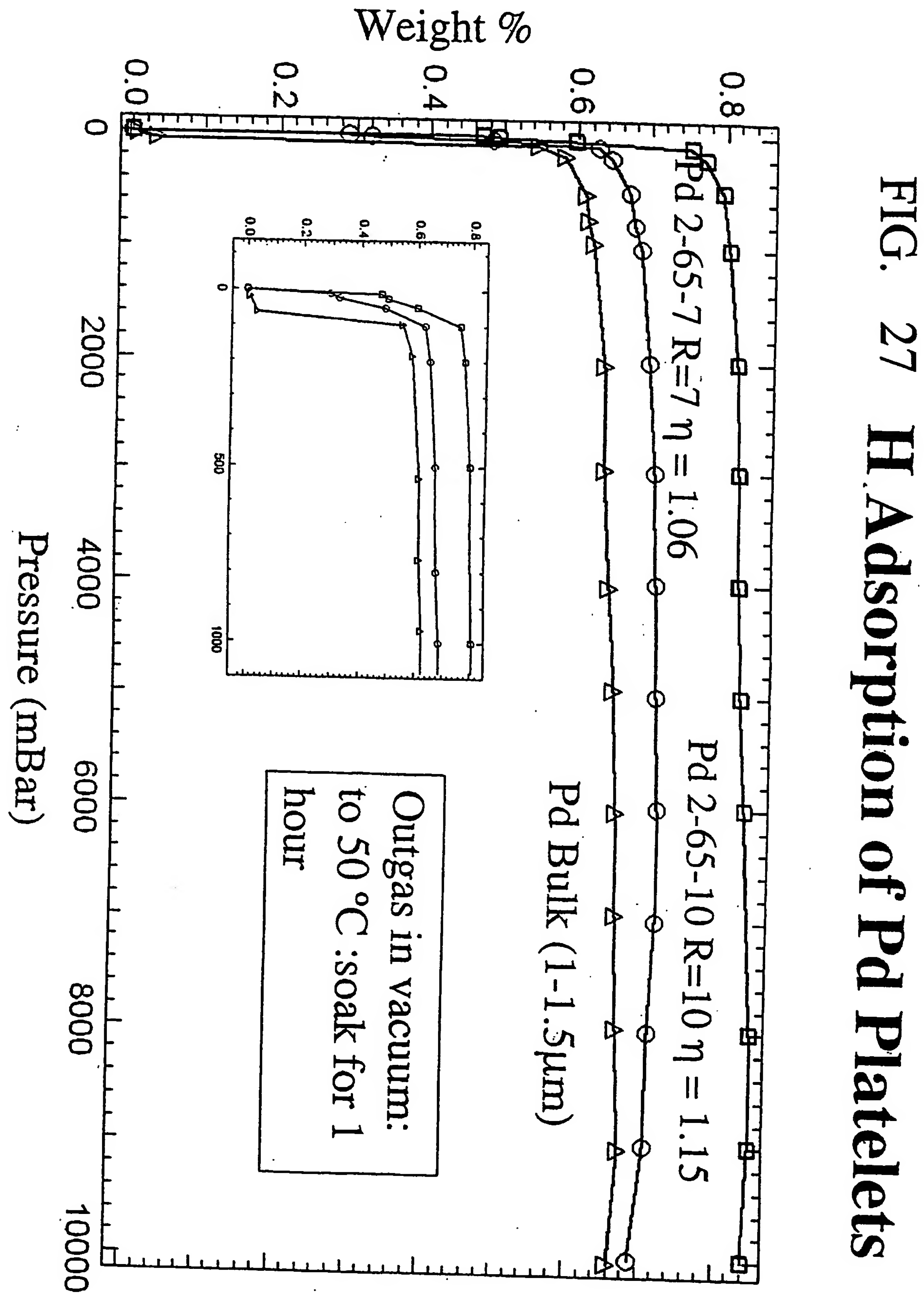
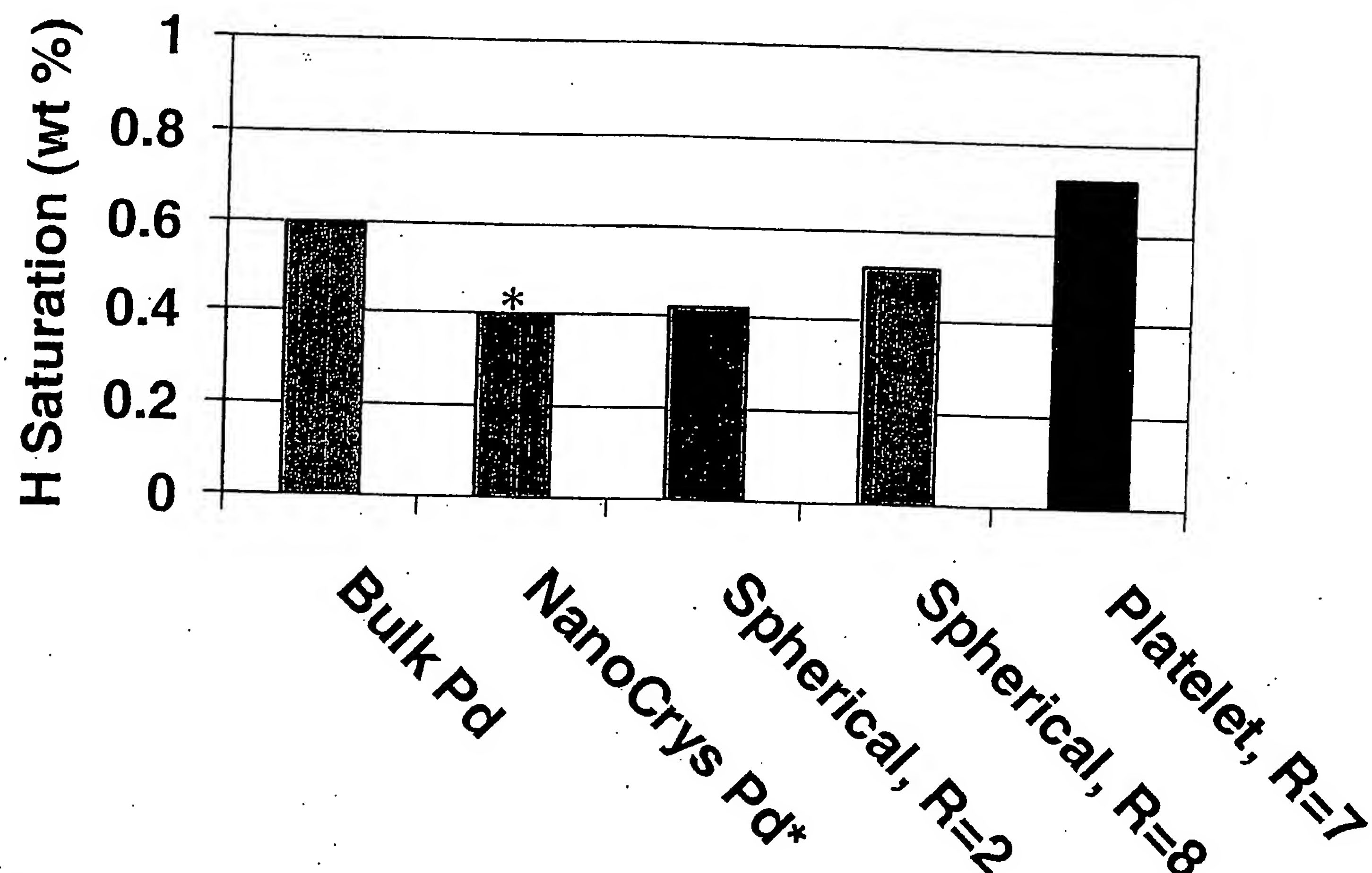


FIG. 28 **Hydrogen Saturation vs Pd Material**



* Kuji, et.al, taken as maximum H/Pd at 0.1 MPa at 353K

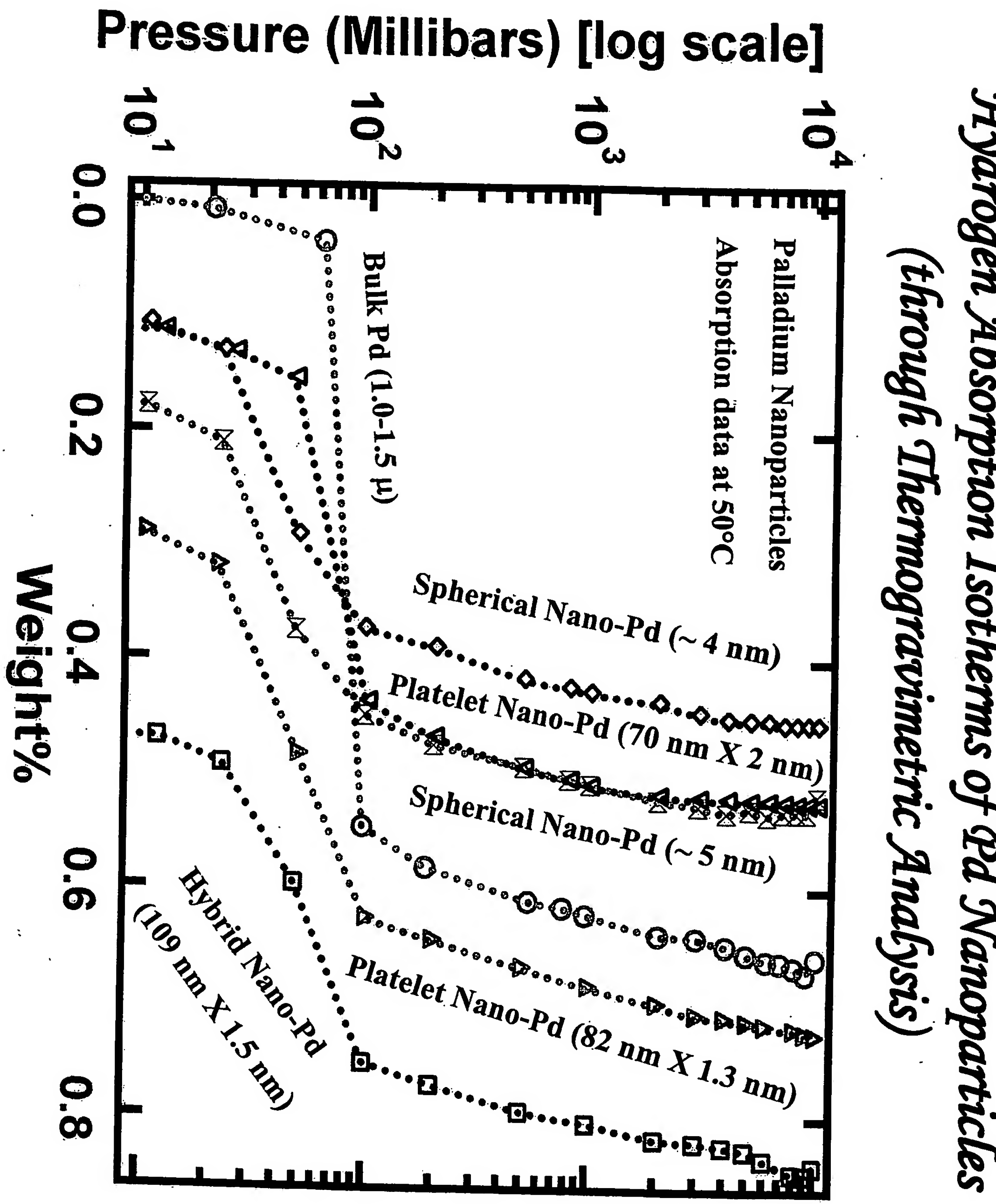

Hydrogen Absorption Isotherms of Pd Nanoparticles
(through Thermogravimetric Analysis)
Pressure (Millibars) [log scale]
10^1
10^2
10^3
10^4
Weight%
0.0
0.2
0.4
0.6
0.8
Palladium Nanoparticles
Absorption data at 50°C
Bulk Pd (1.0-1.5 μ)
Spherical Nano-Pd (~ 4 nm)
Platelet Nano-Pd (70 nm X 2 nm)
Spherical Nano-Pd (~ 5 nm)
Platelet Nano-Pd (82 nm X 1.3 nm)
Hybrid Nano-Pd
(109 nm X 1.5 nm)

FIG. 29

FIG. 30
HRTEM of Platelet Particles

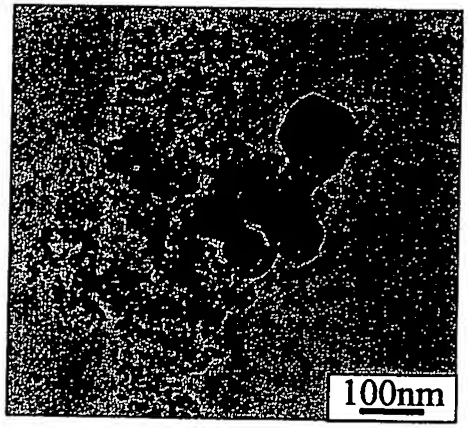


Fig 30a

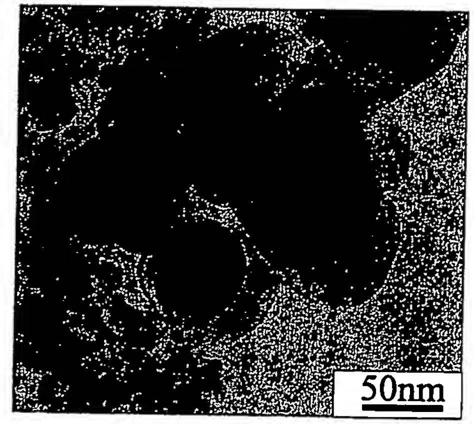


Fig 30b

Mixed (hybride) Platelet Sample

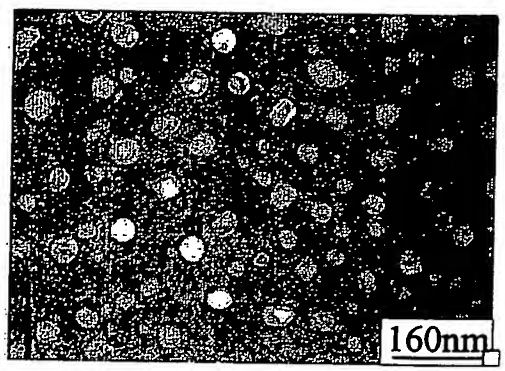


Fig 30c

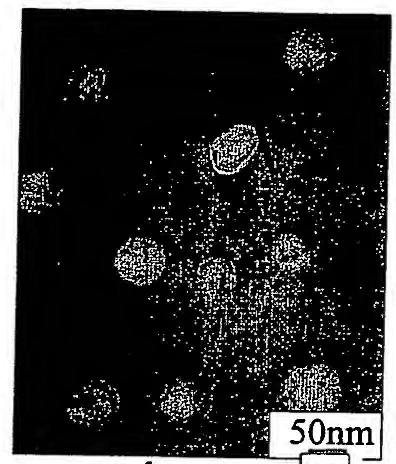


Fig 30d

Platelet Sample average size 70nm X 1.7nm

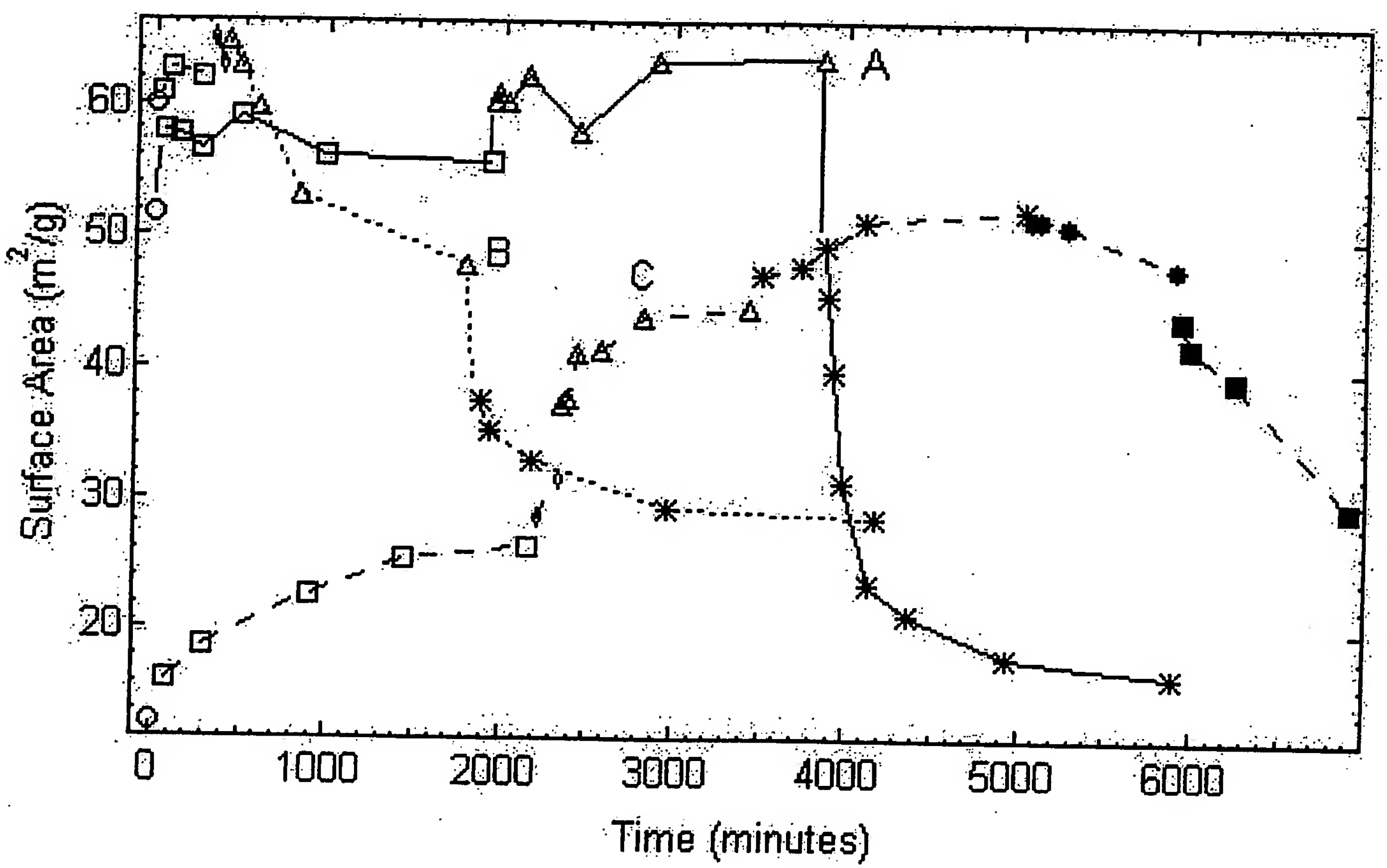
Review of nanoPd Sample tested for Hydrogen Storage

Sample		R	%Pd	d^1	a^2	t^3
Reverse Micelle Synthesis						
2-35*	spherical	2	95	4		
2-71*	spherical	8	96	5		
2-44	spherical	5	82			
Bilayer Synthesis						
2-65-10	mixed	10	87	5	327	2.8
					109	1.5
3-18	platelet	8	96		70	2
3-33	platelet	6	94		130	2.6

R = [water]/[Surfactant], 1= diameter of spherical particle, 2 = face size of platelet particle, and 3 = thickness of platelet particle in nm. * Samples washed with hydrazine

FIG. 31

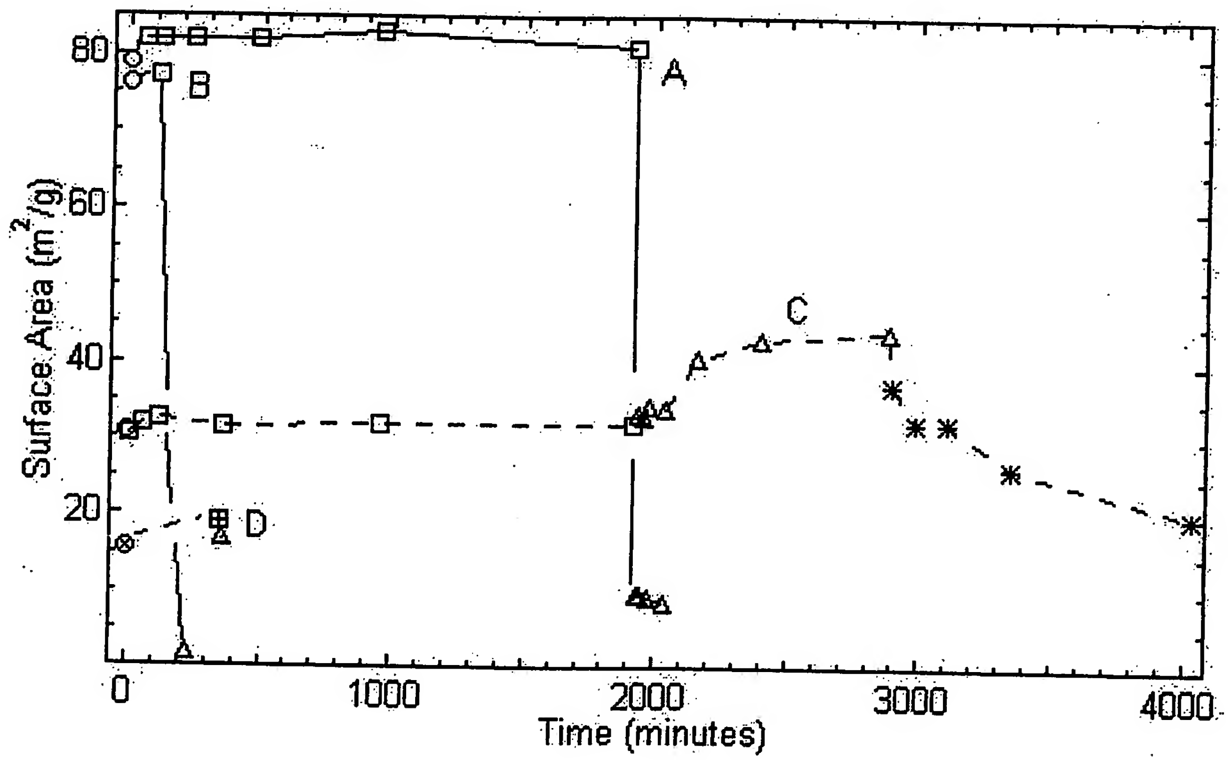
Sintering of Platelet Particles



Surface area vs. heating time for sample synthesized by bilayers. Samples A(sample 3-18) and B(sample 3-33) consist of only platelets. Sample C(sample 2-65-10) is a mix of platelets and spherical particles. Heating temperatures are O = room temperature, □ = 50 °C, ◇ = 75 °C, △ = 100 °C, ✳ = 150 °C, ● = 200 °C. ■ = 250 °C.

FIG. 32

Sintering of Spherical Particles



Surface area vs. heating time for spherical particles synthesized via reverse micelles. A(sample 2-44) and B(sample 2-35) = not washed with hydrazine hydrate. C(sample 2-71) and D(sample 2-35) = washed with hydrazine hydrate. Lines B and D are both of sample 2-35. Heating temperatures are O = room temperature, □ = 50 °C, △ = 100 °C, and ✱ = 150 °C.

FIG. 33

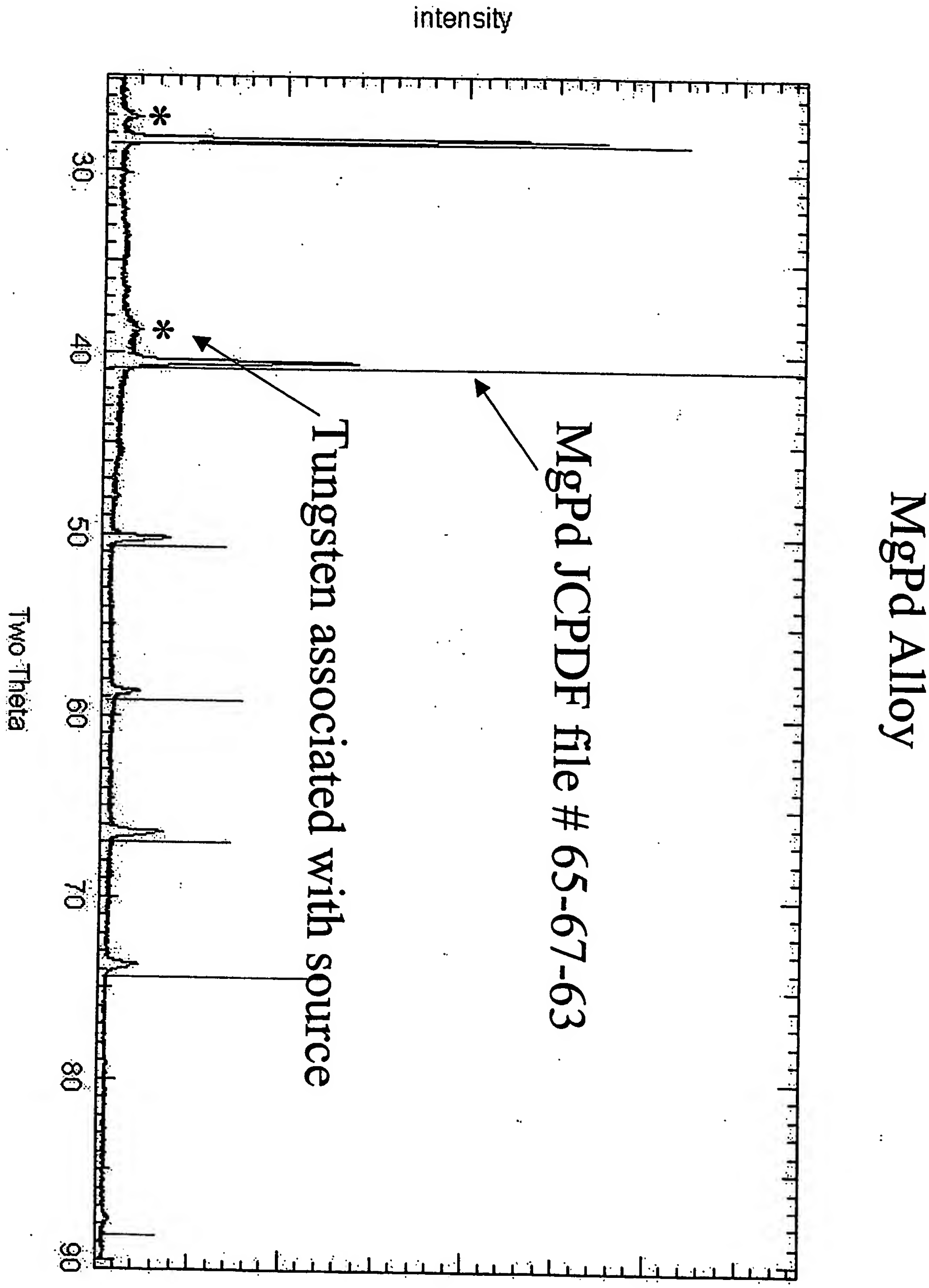
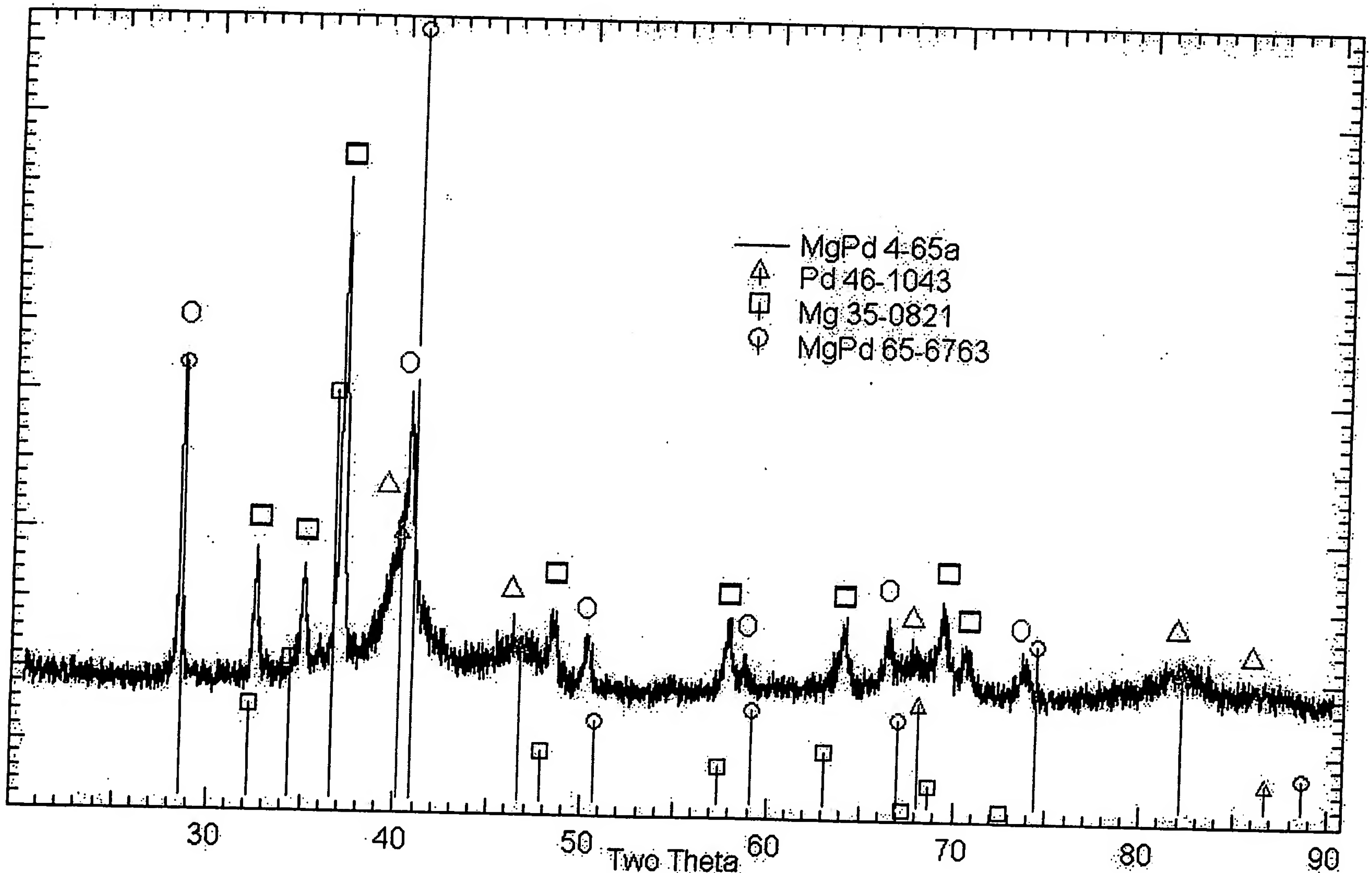

MgPd Alloy
intensity
MgPd JCPDF file # 65-67-63
Tungsten associated with source
*
*
30
40
50
60
70
80
90
Two Theta

FIG. 34

MgPd Alloy with Mg and Pd Metal



It is believed that excess Mg in the reaction lead to the formation of MgPd alloy along with metallic Pd and Mg.

FIG. 35